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NATIONAL WATER QUALITY NETWORK.
REPORT ON REFERENCE SAMPLE TYPE 2, BD-4

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1963

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National Water Quality Network

REPORT ON
REFERENCE SAMPLE
TYPE 2, BD-4

1963

Water Quality Section 1014 Broadway Cincinnati, Ohio

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U.S. Department of
Health, Education and Welfare
PUBLIC HEALTH SERVICE

Participants in Study of Type II, BD-4

(Distributed May 10, 1963)

Massachusetts Department of
Public Health
University of Massachusetts
Amherst, Massachusetts

Bureau of Water Supply
Purification Division
Baltimore, Maryland

U. S. Army Corps of Engineers
Western Virginia Area Office
Berryville, Virginia

Idaho Department of Health
Boise, Idaho

Boulder Canyon Project
Water Treatment Plant
Boulder City, Nevada

Brownsville Public Utilities
Brownsville, Texas

Erie County Health Department
Buffalo, New York

Cairo Water Company
Cairo, Illinois

Missouri Utilities Company
Cape Girardeau, Missouri

West Virginia Division of Water
Resources
Charleston, West Virginia

Tennessee Valley Authority
Stream Pollution Laboratory
Chattanooga, Tennessee

St. Louis Water Department
Chesterfield, Missouri

Cincinnati Water Filtration Plant
Cincinnati, Ohio

Columbus Water Department
Columbus, Georgia

Water Works Park
Filtration Plant
Detroit, Michigan

Duluth Water, Gas, and Sewage
Treatment Department
Lakewood Laboratory
Duluth, Minnesota

Evansville Water Department
Evansville, Indiana

Ohio Valley Electric Corporation
Addison, Ohio

Gary-Hobart Water Company
Gary, Indiana

Grand Junction Filtration Plant
Grand Junction, Colorado

Hagerstown Water Department
Hagerstown, Maryland

National Water Quality Network Report

Indiana State Board of Health Indianapolis, Indiana	Raritan Bay Project Raritan Arsenal Metuchen, New Jersey
Minnesota and Ontario Paper Company International Falls, Minnesota	State Water Resources Laboratory Wesleyan University Middletown, Connecticut
Columbus, Mississippi Mississippi State Board of Health Jackson, Mississippi	Milwaukee Water Department Milwaukee, Wisconsin
Delta, Louisiana Pearl River Project Jackson, Mississippi	State Board of Health New Orleans, Louisiana
Kansas City Board of Public Utilities Kansas City, Kansas	North Augusta Water Department North Augusta, South Carolina
Service Division West Point Manufacturing Company Longdale, Alabama	Nowata Water Department Nowata, Oklahoma
Lawrence Experiment Station Lawrence, Massachusetts	Metropolitan Utilities District Omaha, Nebraska
Lewiston Water Treatment Plant Lewiston, Idaho	Peoria Water Works Company Peoria, Illinois
Louisville Water Company Filter Plant Louisville, Kentucky	Pittsburgh Filtration Plant Pittsburgh, Pennsylvania
Pennsylvania Power and Light Company Martins Creek, Pennsylvania	South Pittsburgh Water Company Pittsburgh, Pennsylvania
Chevrolet Motors Division Massena, New York	Port Huron Sewage Treatment Plant Port Huron, Michigan
Memphis Water Department Memphis, Tennessee	Oregon State Board of Health Portland, Oregon
	Washington State University School of Engineering Pullman, Washington

Reference Sample Type II, BD-4

Richland Sewage Treatment Plant
Richland, Washington

Montana-Dakota Utilities Company
Sidney, Montana

St. Joseph Water Company
St. Joseph, Missouri

Northeast Colorado Health Department
Sterling, Colorado

St. Paul Sanitary District
St. Paul, Minnesota

St. Louis County Water Department
University City, Missouri

Saulte Ste. Marie Water Department
Saulte Ste. Marie, Michigan

Dalecarlia Filtration Plant
Washington, D. C.

West Nebraska Branch Laboratory
Nebraska State Department of Health
Scottsbluff, Nebraska

Aluminum Company of America
Wenatchee, Washington

Yankton Water Department
Yankton, South Dakota

Washington State Department of Health
Seattle, Washington

Arizona Water Company
Yuma, Arizona

INTRODUCTION

Much of the physical and chemical data accumulated by the PHS National Water Quality Network are the result of the cooperative efforts of many laboratories located at or near the sampling sites. Because these analyses originate from so many different sources, it is essential that they be comparable as to accuracy. The reference sample technique is a means by which this objective can be achieved. Reference samples are submitted periodically to each of the cooperating laboratories to assure continued accuracy of the data submitted.

REPORT ON THE REFERENCE SAMPLES

TYPE II, BD-4

Sample Type II, BD-4 is the fourth in a series of standard samples representative of the "demand" type analyses being reported to the network. Because of changes which occur with time, it is practically impossible to provide standard samples for the direct determination of these parameters; therefore an indirect approach was used, as in previous samples of this type. By preparing standard solutions which produce measurable and precise effects when added to raw samples, errors in technique, procedure, or other factors which affect these tests can be discovered, thus alerting the cooperating laboratories and the program to possible sources of error.

The results are reported in Table 2 and in the bar graphs. The dotted lines on the graphs represent limits of accuracy which are acceptable to the Program for this sample. Selection of these limits was influenced by the accuracy with which each test can be performed, as determined by "Standard Methods," as well as by the needs of the Program. In most cases, those laboratories whose reports were outside the acceptable range were notified and requested to review their procedures in order to determine the reasons for the discrepancies. Each discussion is followed by a tabulation of sources of error or of pitfalls for the various determinations. In addition, assistance with laboratory procedures is available to the Network laboratories from the Public Health Service, through its Regional Offices or the Water Quality Section. *

*Water Quality Section, Basic Data Branch, Division of Water Supply and Pollution Control, 1014 Broadway, Cincinnati 2, Ohio.

DISCUSSION OF RESULTS

Statistical comparisons in this report were developed from the deviations from known quantities added to the sample. Table 1 is a summary of the expected accuracy for the various tests, according to "Standard Methods for the Examination of Water and Wastewater," and of the ranges considered acceptable by the Water Quality Network for this reference sample.

Laboratories reporting values outside the range of acceptability should investigate their procedures for sources of error:

1. Are samples well mixed to assure true aliquots?
2. Are standard solutions checked frequently?
3. Are the reagents too old?
4. Are sample sizes adequate for maximum accuracy?
5. Are weighings made carefully?
6. Are standard curves checked frequently?
7. Are results reported correctly?

A thorough review of the details in each procedure may disclose errors which have become habitual and thus escape notice during routine operations.

Recent editions of "Standard Methods" give the expected precision and accuracy for most tests within the range of concentration normally encountered in water analysis. These standards of accuracy should be attainable by most laboratories performing these routine examinations. The additional errors, allowable for the Network Program, are intended only as a guide and are not to be considered as ultimate goals in laboratory accuracy.

Table 1. Acceptable Limits of Accuracy

	Standard Methods	National Water Quality Network
pH	± 0.1 unit	± 0.2 unit
Dissolved Oxygen	± 0.1 mg/l	± 0.2 mg/l
Biochemical Oxygen Demand	± 0.11 mg/l	± 0.3 mg/l
Chemical Oxygen Demand	± 1.6 mg/l	± 5.8 mg/l
Ammonia Nitrogen (direct Nessler)	± 0.01 mg/l	± 0.05 mg/l

HYDROGEN ION CONCENTRATION (pH) - 8.3

Solution A of this sample consisted of a sterile solution of a Clark and Lubs buffer. The pH was verified at the SEC by measurement with three carefully standardized pH meters. Of the 57 laboratories reporting this analysis, 49 fell within the acceptable limit of ± 0.2 units from the known value, and all results were within twice the acceptable limit. Nineteen results were perfect. Overall performance was good, but should have been better, since the sample contained no interference that might affect either electrometric or colorimetric measurements.

SUMMARY OF RESULTS

Amount added	8.3 pH units
Mean	8.2 pH units
Median	8.2 pH units
50% range	± 0.1 pH unit
Number of analyses	156
Average deviation from amount added	± 0.12 pH unit
Range	7.9 - 8.7 pH units

COMPARISON WITH PREVIOUS SAMPLE**Percent of Labs Within Acceptable Limits**

I-BD-7	87%
II-BD-4	86%

Percent Beyond Twice Acceptable Limits

I-BD-7	5%
II-BD-4	0%

Percent Perfect Results

I-BD-7	35%
II-BD-4	33%

REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS

1. Possible over-age of colorimetric pH indicators or standards.
2. Improper standardization of pH meter; outdated buffer solutions.
3. Improper rinsing of electrodes between samples.



LABORATORY NUMBER

DISSOLVED OXYGEN - 2.3 mg/l

The method used for evaluating the dissolved oxygen determination was the same as in previous samples. A solution which produces a calculated reduction in dissolved oxygen was added to one of a pair of duplicate samples. If the test was performed properly, the decrease in DO should have been 2.3 mg/l.

Of the 55 laboratories reporting this analysis, 41 submitted results within acceptable limits, eight of which submitted perfect results. Three results were beyond twice the acceptable limit. Except for two gross errors, the results are generally excellent and indicate no significant difficulties within this test.

SUMMARY OF RESULTS

Amount added	2.3 mg/l
Mean	2.2 mg/l
Median	2.2 mg/l
50% range	± 0.1 mg/l
Number of analyses	147
Average deviation from amount added	± 0.22 mg/l
Range	1.0 - 3.1 mg/l

COMPARISON WITH PREVIOUS SAMPLE**Percent of Labs Within Acceptable Limits**

II-BD-3	77%
II-BD-4	75%

Percent Beyond Twice Acceptable Limits

II-BD-3	3%
II-BD-4	5%

Percent Perfect Results

II-BD-3	10%
II-BD-4	15%

REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS

High Results

1. Too much of Solution B added.
2. Normality of standard thiosulfate low.
3. Faint endpoint due to deteriorated starch solution.
4. Interference from nitrites - i. e., omission of sodium azide from alkaline iodide solution.
5. Exposure to air after alkaline iodide addition.

Low Results

1. Too little of Solution B added.
2. Normality of standard thiosulfate high.
3. Warming of sample before reagent addition.
4. Failure to mix sample completely after addition of alkaline iodide.



BIOCHEMICAL OXYGEN DEMAND - 2.4 mg/l

To evaluate the BOD test, a specific amount of Solution C was added to one portion of a split sample of river water. This addition theoretically increased the BOD of the river water 2.4 mg/l. It is recognized that the BOD values are not absolute since they are the result of biological activity and are subject to variables such as numbers and varieties of microorganisms present in the raw water. A generous allowance, therefore, has been made in the acceptable limits for this measurement. In addition, the correct value is defined as any figure between 2.1 and 2.4 mg/l, since lack of active biological forms or deficiency of nutrients such as nitrogen and phosphorus in the raw water tends to produce a result lower than the theoretical result.

Forty-six laboratories reported this analysis. Twenty-eight results were within the acceptable limits, six were considered perfect, and eight results were beyond twice the acceptable limits. The results are evenly distributed about the known value and show no pronounced tendency toward high or low values.

In comparing these results with those of the previous sample it appears that accuracy has declined. This conclusion is not altogether justified, however, since Analytical Reference Service studies show that when the number of participants greatly increases, the percentage but not the number of acceptable results tends to decrease. A possible explanation is that some of the more recent participants have had less experience with the determinations.

The results of this sample may be considered generally excellent since this test, as mentioned earlier, is subject to many variables.

SUMMARY OF RESULTS

Amount added	2.4 mg/l
Mean	2.4 mg/l
Median	2.5 mg/l
50% range	+ 0.4 mg/l
Number of analyses	108
Average deviation from amount added	+ 0.69 mg/l
Range	0.4 - 5.4 mg/l

COMPARISON WITH PREVIOUS SAMPLE

Percent of Labs Within Acceptable Limits

II-BD-3	78%
II-BD-4	61%

Percent Beyond Twice Acceptable Limits

II-BD-3	11%
II-BD-4	17%

Percent Perfect Results

II-BD-3	37%
II-BD-4	13%

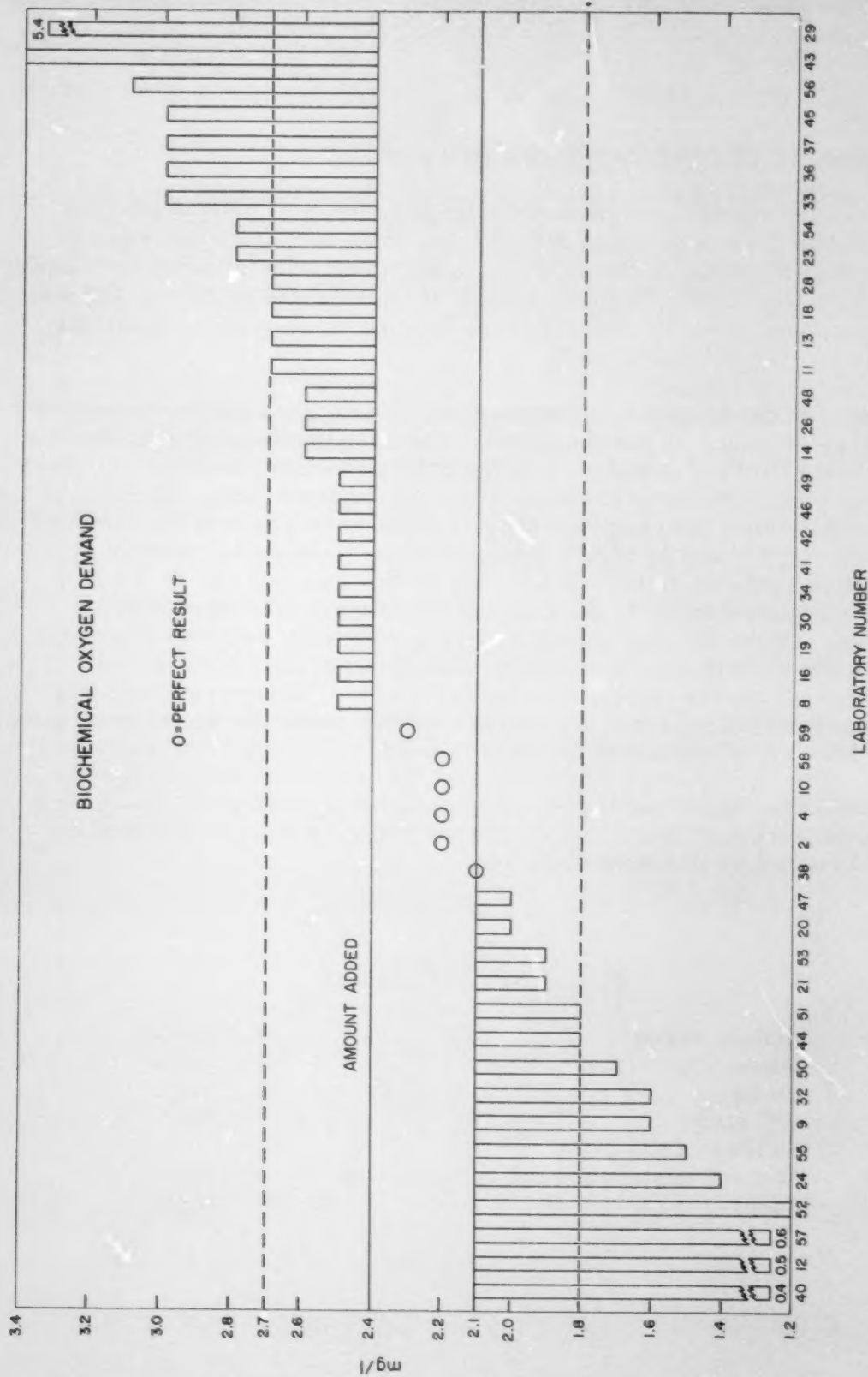
REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS

High Results

1. Initial DO measurement too low.
2. Incubation of 5-day sample at temperature above 20°C.
3. Improper sampling.
4. Too much of Solution C added.
5. Failure to deaerate cold sample, i. e. , when oxygen content is above saturation.

Low Results

1. Initial DO measurement too high.
2. Lack of seed organisms.
3. Improper sampling.
4. Incubation of 5-day sample at temperature below 20°C.
5. Lack of nutrient materials.



CHEMICAL OXYGEN DEMAND - 38.4 mg/l

The evaluation of the COD test was accomplished by using a simpler procedure than in previous demand type reference samples. Instead of adding a solution to river water, a direct determination on the sample solution was made. The only source of interference in the sample was 7.6 mg/l chloride for which a correction had to be made if the silver sulfate catalyst was not used.

In spite of the simplicity of the sample, it was again decided to consider a range of values as being correct. The sample contained glucose which is rarely oxidized completely by the COD procedure, tending to produce results below the theoretical results. On the other hand, the Network procedure does not require a reagent blank to be run with the samples, which would result in higher values if contaminants were present in the distilled water or sulfuric acid. The theoretical value of 38.4 was accordingly expanded to the range of 37-39 mg/l COD for a correct result. Of the 39 laboratories reporting this test, only 23 were within the acceptable limits, seven were considered perfect results, and eight were beyond twice the acceptable limits. The general tendency was toward high results, indicating possible contamination of apparatus or reagents, particularly the sulfuric acid.

It should be emphasized again, that scrupulous attention to cleanliness of glassware and standardization of the reagents must be followed for good results on this determination.

SUMMARY OF RESULTS

Amount added	38.4 mg/l
Mean	45 mg/l
Median	43 mg/l
50% range	$\pm$ 6 mg/l
Number of analyses	95
Average deviation from amount added	$\pm$ 9 mg/l
Range	0 -100 mg/l

COMPARISON WITH PREVIOUS SAMPLE

Percent of Labs Within Acceptable Limits

II-BD-3	72%
II-BD-4	59%

Percent Beyond Twice Acceptable Limits

II-BD-3	12%
II-BD-4	21%

Percent Perfect Results

II-BD-3	20%
II-BD-4	18%

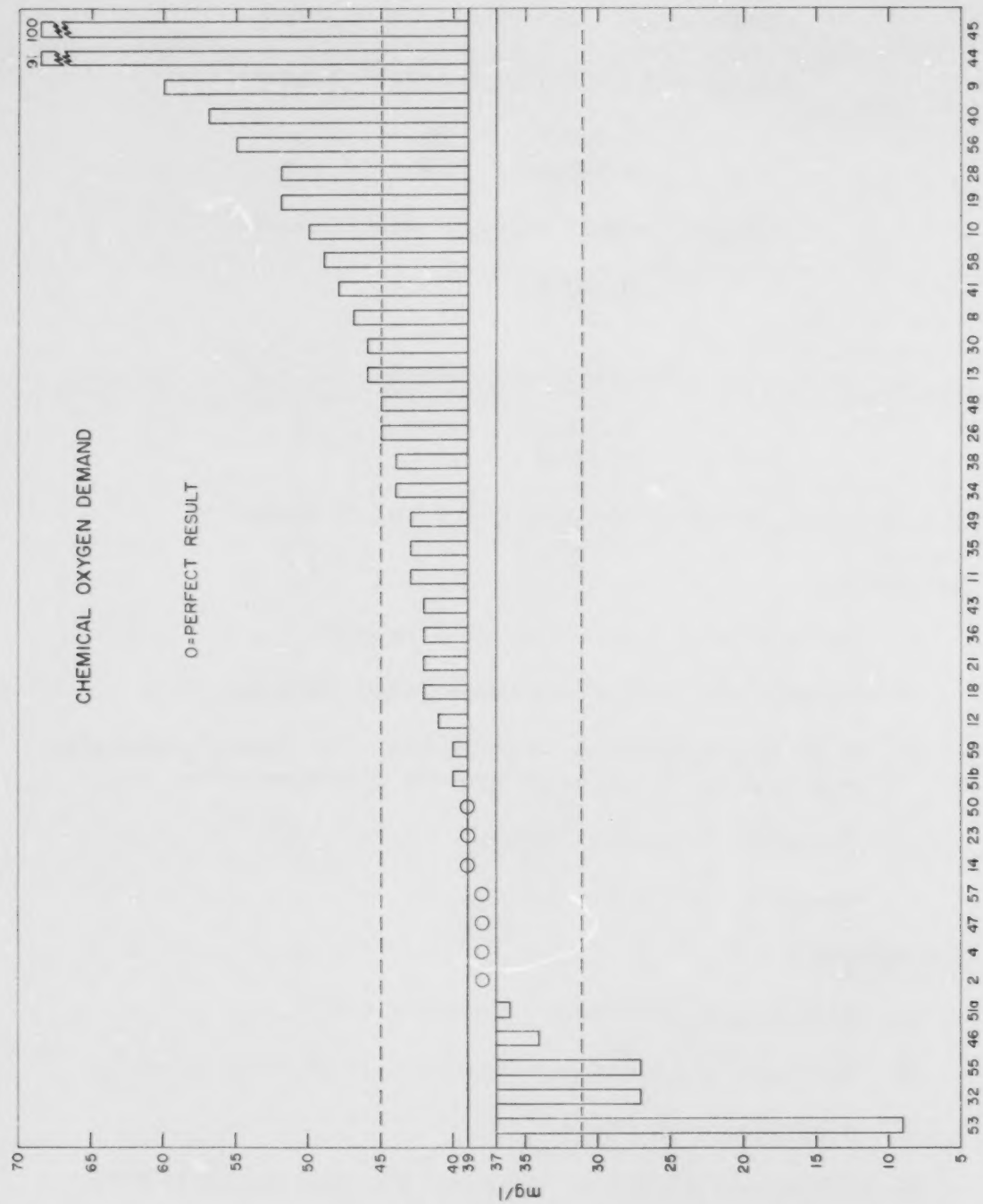
REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS

High Results

1. Normality of dichromate solution too low.
2. Normality of ferrous ammonium sulfate too high.
3. Extraneous organic material present, i. e., greasy glassware, impure reagents, bacterial growths in dilution water.
4. Too much of Solution C added.
5. Failure to correct for chloride.

Low Results

1. Normality of dichromate solution too high.
2. Normality of ferrous ammonium sulfate too low.
3. Insufficient reflux time.
4. Insufficient H_2SO_4 i. e., less than 50% total volume in flask.
5. Sample too warm when titrated with ferrous ammonium sulfate. (destruction of indicator)
6. Not enough of Sample C added.



AMMONIA NITROGEN - 0.3 mg/l N

This test was performed in the usual manner by adding a measured amount of sample solution to one portion of a split sample of river water, thereby increasing the ammonia content by a known amount.

The data system used by the National Water Quality Network does not provide for reporting ammonia-nitrogen values of less than a tenth mg/l, and participating laboratories are instructed to round off values to the nearest tenth mg/l. Under this system, it would be unreasonable to require accuracy greater than one-tenth mg/l. On the other hand, this degree of accuracy makes a $\pm 33\%$ error appear acceptable while actually it represents poor accuracy for a sample containing no interferences. An arbitrary accuracy of ± 0.05 mg/l is inherent in the freedom to round off to the nearest tenth mg/l, and this value, therefore, is used as the acceptable limit for this sample.

Forty-three laboratories reported this analysis and only 17 results were within the acceptable limits of accuracy. The nine laboratories that submitted high results beyond twice the acceptable limits should make a careful check for possible ammonia contamination of the atmosphere and glassware in the laboratory. (The buffer for the hardness determination customarily contains a high concentration of ammonia.)

SUMMARY OF RESULTS

Amount added	0.3 mg/l
Mean	0.4 mg/l
Median	0.3 mg/l
50% range	± 0.1 mg/l
Number of analyses	109
Average deviation from amount added	± 0.14 mg/l
Range	0.2 - 1.0 mg/l

COMPARISON WITH PREVIOUS SAMPLE**Percent of Labs Within Acceptable Limits**

II-BD-3	68%
II-BD-4	40%

Percent Beyond Twice Acceptable Limits

II-BD-3	8%
II-BD-4	21%

Percent Perfect Results

II-BD-3	0%
II-BD-4	40%

REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS**High Results**

1. Too much of Solution C added.
2. Contamination by extraneous ammonia, i. e. , ammonia in distilled water, laboratory fumes, etc.
3. Incorrect standards.

Low Results

1. Too little of Solution C added.
2. Incorrect standards.
3. Weak Nessler reagent.

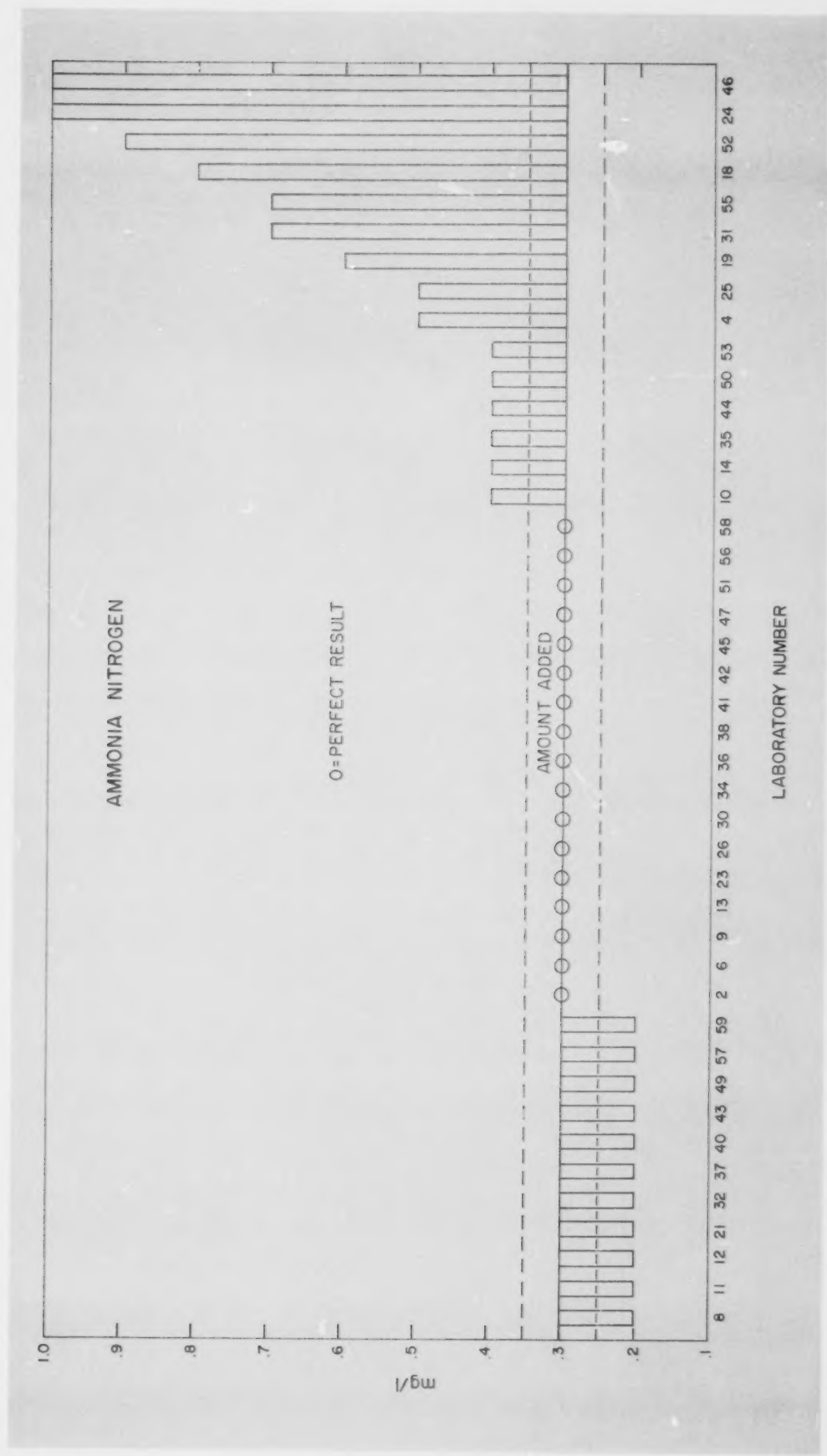


Table 2. SUMMARY OF RESULTS
REFERENCE SAMPLE TYPE II-BD-4

Analyses performed	pH		DO		BOD		COD		NH ₃ /N	
	8.3 mg/l		2.3 mg/l		2.4 mg/l		38.4 mg/l		0.30 mg/l	
Amount added	Avg. dev. from am't added		Average result		Avg. dev. from am't added		Average result		Avg. dev. from am't added	
Laboratory number	Average result	Avg. dev. from am't added	Average result	Avg. dev. from am't added	Average result	Avg. dev. from am't added	Average result	Avg. dev. from am't added	Average result	Avg. dev. from am't added
1	8.1	0.2	2.5	0.23	---	---	---	---	---	---
2	8.2	0.1	2.3	0.10	2.2	0.2	38	0.3	0.3	0.03
3	8.1	0.2	---	---	---	---	---	---	---	---
4	8.0	0.3	2.2	0.1	2.2	0.2	38	1.7	0.5	0.2
5	8.3	0.0	2.0	0.3	---	---	---	---	---	---
6	8.3	0.0	2.2	0.1	---	---	---	---	0.3	0.0
7	8.2	0.1	2.1	0.2	---	---	---	---	---	---
8	8.3	0.0	2.3	0.03	2.5	0.1	47	8.0	0.2	0.1
9	8.3	0.0	2.4	0.10	1.6	0.8	60	20.7	0.3	0.0
10	8.0	0.3	2.1	0.23	2.2	0.3	50	11.3	0.4	0.1
11	---	---	2.3	0.23	2.7	0.33	43	4.3	0.2	0.1
12	8.3	0.0	2.2	0.1	0.5	1.9	41	2.0	0.2	0.1
13	8.1	0.2	2.4	0.13	2.7	0.27	46	7.0	0.3	0.0
14	8.3	0.0	2.2	0.1	2.6	0.23	39	0.3	0.4	0.05
15	8.0	0.3	2.7	0.47	---	---	---	---	---	---

16	8.1	0.2	2.2	0.1	2.5	0.1	---	---	---	---
17	8.2	0.1	---	---	---	---	---	---	---	---
18	8.1	0.2	2.3	0.07	2.7	0.3	42	3.0	0.8	0.5
19	8.2	0.1	2.7	0.37	2.5	0.1	52	13.0	0.6	0.3
20	8.0	0.3	2.2	0.35	2.0	0.45	---	---	---	---
21	8.3	0.0	2.4	0.10	1.9	0.5	42	3.0	0.2	0.1
22	8.3	0.0	---	---	---	---	---	---	---	---
23	8.3	---	2.2	0.1	2.8	0.4	39	0.0	0.3	0.03
24	8.2	0.1	2.2	0.07	1.4	1.03	---	---	1.0	0.73
25	8.4	0.1	---	---	---	---	---	---	0.5	0.2
26	8.2	0.1	1.9	0.45	2.6	0.25	45	6.5	0.3	0.0
27	8.4	0.07	2.2	0.05	---	---	---	---	---	---
28	8.3	0.03	2.2	0.07	2.7	0.3	52	13.0	---	---
29	8.3	0.03	2.7	0.43	5.4	3.03	---	---	---	---
30	8.3	0.0	2.2	0.15	2.5	0.13	46	7.3	0.3	0.05
31	8.0	0.3	3.1	0.8	---	---	---	---	0.7	0.4
32	8.3	0.0	2.3	0.07	1.6	0.83	27	10.0	0.2	0.1
33	8.1	0.2	2.6	0.3	3.0	0.6	---	---	---	---
34	8.2	0.1	2.1	0.23	2.5	4.5	44	5.0	0.3	0.0
35	8.2	0.1	2.4	0.15	---	---	43	4.7	0.4	0.1
36	8.1	0.2	2.2	0.1	3.0	0.57	42	3.0	0.3	0.0

Analyses performed		pH		DO		BOD		COD		NH ₃ /N	
Amount added		8.3 mg/l		2.3 mg/l		2.4 mg/l		38.4 mg/l		0.30 mg/l	
Laboratory number	Average result	Avg. dev. from am't added	Average result	Avg. dev. from am't added	Average result	Avg. dev. from am't added	Average result	Avg. dev. from am't added	Average result	Avg. dev. from am't added	Average result
37	8.0	0.3	2.3	0.03	3.0	0.7	---	---	0.2	0.1	0.1
38	8.2	0.1	1.9	0.4	2.1	0.87	44	5.0	0.3	0.0	0.0
39	8.3	0.03	2.0	0.3	---	---	---	---	---	---	---
40	8.4	0.1	2.1	0.23	0.4	2.0	57	18.0	0.2	0.1	0.1
41	8.1	0.2	1.0	1.27	2.5	0.13	48	9.0	0.3	0.0	0.0
42	8.4	0.07	2.3	0.1	2.5	0.1	---	---	0.3	0.0	0.0
43	8.5	0.2	2.2	0.1	3.4	1.0	42	3.0	0.2	0.1	0.1
44	8.4	0.1	2.5	0.23	1.8	0.6	91	52.3	0.4	0.1	0.1
45	8.3	0.0	2.0	0.33	3.0	0.6	100	61.0	0.3	0.0	0.0
46	8.3	0.0	2.1	0.2	2.5	0.17	34	2.7	1.0	0.7	0.7
47	8.2	0.1	2.0	0.33	2.0	0.43	38	0.0	0.3	0.0	0.0
48	8.7	0.4	2.0	0.27	2.6	0.2	45	6.3	---	---	---
49	7.9	0.4	2.1	0.2	2.5	0.13	43	4.5	0.2	0.1	0.1
50	8.2	0.1	2.4	0.30	1.7	0.75	39	0.0	0.4	0.1	0.1
51	8.2	0.1	2.1	0.2	1.8	0.6	(a) 36(b) 40	(a) 0.5(b) 1.0	0.3	0.0	0.0
52	8.4	0.1	2.2	0.07	1.2	1.2	---	---	0.9	0.6	0.6

53	8.2	0.07	1.8	0.5	1.9	0.5	9	28.0	0.4	0.1
54	>7.6	---	2.1	0.17	2.8	0.37	---	---	---	---
55	8.3	0.0	2.2	0.1	1.5	0.83	27	10.3	0.7	0.37
56	8.2	0.1	2.2	0.13	3.1	0.67	55	16.0	0.3	0.03
57	8.2	0.1	2.2	0.1	0.6	1.77	38	0.0	0.2	0.1
58	8.3	0.0	2.3	0.07	2.2	0.2	49	10.0	0.3	0.07
59	8.3	0.0	2.2	0.1	2.3	0.63	40	1.3	0.3	0.1

Mean	8.2	2.2	2.4	45	0.4
Median	8.2	2.2	2.5	43	0.3
Range	7.9-8.7	1.0-3.1	0.4-5.4	9-100	0.2-1.0